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(54) Flame retardant mixture and resinous compositions including the mixture

(57) A flame retardant composition for resinous compositions, especially for mixtures of polyphenylene ethers and styrene resins, comprises a mixture of triaryl phosphates including at least one such phosphate wherein 1 or 2 of its 3 aryl groups are mesityl groups and its remaining group or groups are independently selected from phenyl and xylyl groups. In the resinous composition, the flame retardancy of the mixture per unit weight of phosphorus is greater than that of either triphenyl phosphate (TPP) or trimesityl phosphate (TMP) per se.

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SPECIFICATION

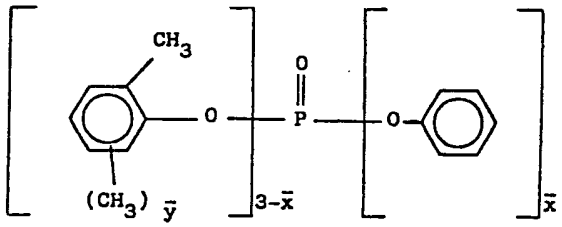
Flame retardant mixture and resinous compositions including the mixture

This invention relates to a flame retardant mixture comprising a mixture of triaryl phosphates and to a resinous composition comprising a normally flammable resinous material and the flame retardant mixture.

Haaf, U. S. Patent 3,639,506, discloses a blend of polyphenylene ether and a styrene resin containing a flame retardant combination comprising an aromatic phosphate and an aromatic halogen compound. The Haaf patent discloses a wide variety of phosphates for use as the aromatic phosphate component of the blend, indicates a preference for triaryl phosphates, and states that the most preferred phosphate is triphenyl phosphate. Copper, U.S. Patent 3,883,613 discloses that trimesityl phosphate functions very effectively as a flame retardant *per se* in compositions of a polyphenylene ether and a styrene resin.

It has now been found that effective flame retardancy is provided by a new mixture of triaryl phosphates, which includes at least one such phosphate wherein 1 or 2 of its 3 aryl groups are mesityl groups and its remaining group or groups are independently selected from phenyl and xylyl groups. It has further been found that, in resinous compositions containing a normally flammable resin material and the mixture, the flame retardancy of the mixture, per unit weight of phosphorus, is greater than that of either triphenyl phosphate (TPP) or trimesityl phosphate (TMP) *per se*. Advantageously, this increased flame retardancy is obtained where the resin comprises a mixture of polyphenylene ethers and styrene resins, which are known in the art and are described in the above-referenced Haaf and Cooper patents and in Cizek, U.S. Patent 3,383,435.

Generally stated, the present invention provides in one aspect thereof a flame retardant mixture comprising a mixture of aromatic phosphates represented by the average formula:



where $\bar{x}$ is a whole or fractional number from slightly more than 0 to slightly less than 3, and $\bar{y}$ is a whole or fractional number from 1 to 2.

In another aspect, this invention provides a resinous composition comprising (A) a normally flammable resinous material and (B) a flame retardant amount of the flame retardant mixture set forth above.

Practice of this invention will be better understood by referring to the following detailed description.

Aromatic phosphates which may be included in the mixture of aromatic phosphates include, for example, triphenyl phosphate (TPP), diphenyl mesityl phosphate (DPMP), dimesityl phenyl phosphate (DMPP), trimesityl phosphate (TMP), trixylyl phosphate (TXP), dixylyl mesityl phosphate (DXMP), dimesityl xylyl phosphate (DMXP), and trimesityl phosphate.

In a preferred embodiment, $\bar{Y}$ is 2 and the flame retardant mixture comprises at least 2 compounds selected from the group consisting of (a) triphenyl phosphate (TPP), (b) diphenyl mesityl phosphate (DPMP), (c) dimesityl phenyl phosphate (DMPP) and (d) trimesityl phosphate (TMP) subject to the proviso that at least one of said two compounds is selected from the group consisting of DPMP and DMPP. Preferably the mixture comprises at least 3 of said compounds, and more preferably all 4 of said compounds.

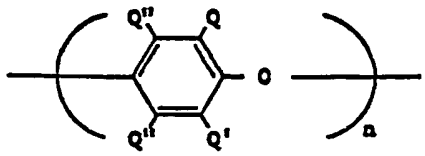
In another preferred embodiment $\bar{y}$ is 1 and the flame retardant mixture comprises at least 2 compounds selected from the group consisting of (a) trixylyl phosphate (TXP), (b) dixylyl mesityl phosphate (DXMP), (c) dimesityl xylyl phosphate (DMXP) and (d) trimesityl phosphate (TMP) subject to the proviso that at least one of said 2 compounds is selected from the group consisting of DXMP and DMXP. Preferably the mixture comprises at least 3 of said compounds, and more preferably 4 of said compounds.

The flame retardant mixture may further include, in addition to the mixture having the above average formula, (isopropyl phenyl) phosphates, e.g. tri(isopropyl phenyl) phosphate, such as commercially available Kronitex K—50.

The resin normally flammable resinous material of the resinous composition includes one or more normally flammable resins which are capable of being improved with respect to flame retardancy by the addition thereto of substituted or unsubstituted triarylphosphates. It is well known in the art that such

resins include for example, polyvinyl chlorides, polyphenylene ethers, cellulosic resins, and many polyesters.

In a preferred embodiment, the normally flammable resinous material comprises
(i) a polyphenylene ether of the formula

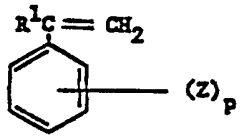


wherein the oxygen ether atom of one unit is connected to the benzene nucleus of the next adjoining unit; Q is a monovalent substituent selected from hydrogen, a hydrocarbon radical, a halohydrocarbon radical having at least two carbon atoms between the halogen atom and the phenol nucleus, a hydrocarbonoxy radical, and a halohydrocarbonoxy radical having at least two carbon atoms between the halogen atom and the phenol nucleus, Q' and Q'' are the same as Q and in addition, halogen, with the proviso that Q, Q' and Q'' are all free of a tertiary alpha-carbon atom and n is a whole number of at least 50; and

(ii) a styrene resin.

Polyphenylene ethers represented by the formula of component (i) above and methods for their formulation may be found in U.S. Patent Nos. 3,306,874 and 3,306,875 of Allan S. Hay and U. S. Patent Nos. 3,257,357 and 3,257,358 of Gelu Stamatoff.

The styrene resin (ii), as is described in the above noted Cizek patent, has at least 25 percent by weight polymer units derived from the compound having the formula:



where R^1 is a hydrogen, (lower)alkyl or halogen; Z is a member selected from the class consisting of vinyl, halogen, and (lower)alkyl; and p is a whole number equal to 0 to the number of replaceable hydrogen atoms on the benzene nucleus. Typical styrene resins include, by way of example, homopolymers such as polystyrene and polychlorostyrene, the modified polystyrenes such as rubber modified polystyrenes (high impact styrenes), and the styrene containing copolymers such as the styrene-acrylonitrile copolymers (SAN), styrene-butadiene copolymers, styrene-acrylonitrile-alpha-alkyl styrene copolymers, styrene-acrylonitrile-butadiene copolymers (ABS), poly-alpha-methyl styrene, copolymers of ethylvinyl benzene and divinyl benzene, and the like. (Lower)alkyl groups contain up to 6 carbon atoms.

A preferred ratio of polyphenylene ether to styrene resin comprises 20 to 80% by weight of the latter. The polyphenylene ether is preferably poly(2,6-dimethyl-1,4-phenylene)ether. The styrene resin is preferably a rubber modified high impact polystyrene as is described in the Cizek patent.

The manner of adding the flame retardant mixture to the normally flammable resinous composition is not critical. Preferably, each component is added as a part of a premix, the latter being passed through an extruder with extrusion temperature being maintained between about 450° and 640°F., dependent upon the composition. The strands emerging from the extruder may be cooled, chopped into pellets, re-extruded, chopped into pellets and molded to a desired shape.

The concentration of the flame retardant mixture in the resinous composition is not critical and is dependent to a large extent upon the degree of flammability of the normally flammable resin composition. Where the last-mentioned composition comprises a polyphenylene ether and a styrene resin, the degree of flammability is dependent to a large extent upon the concentration of the styrene resin and the particular styrene resin used. Lower concentrations of styrene resin or less flammable styrene resins may include a lower concentration of the flame retardant. In general, a small concentration of the flame retardant is desirable, 0.5 to 15 parts per 100 parts of polymer (phr.) generally being acceptable and between 1 and 10 phr being preferred where the styrene content permits.

This invention is further illustrated by the following non-limiting examples.

Preparation of a mixture of mesityl xylyl phosphates from a mixture of polymethylphenols for uses in the Examples.

To a 250 ml flask equipped with a stirrer, reflux condenser, thermometer, and heater was added 396 gm of a mixture of polymethylphenols. The mixture consisted of 75% 2,4,6-trimethylphenol, 23% 2,4 and 2,6-dimethylphenols and 2,3,6-trimethylphenol and anisoles. The phenolics were combined with 153 g of phosphorus oxychloride and 8 gm of magnesium chloride at 25°C. This mixture was

heated to 250°C for six hours and hydrogen chloride was continuously evolved. After purging the reaction mass with nitrogen, it was purified by vacuum distilling unreacted phenolics.

Gas chromatographic analysis indicated the still pot contained 95% of a mixture of triaryl phosphates after the phenolics were removed and the yield of mixed mesityl xylyl phosphates was 78%. The product mixture is transparent and glassy and has a pour point near 80°C. It is hereinafter designated the "mesityl xylyl phosphate mixture."

EXAMPLE 1

Poly(2,6-dimethyl-1,4-phenylene)ether, 400 parts; 600 parts of rubber modified high impact polystyrene Foster Grant 834; 5 parts of diphenyl decyl phosphite, 15 parts of polyethylene, and 130 parts of the mesityl xylyl phosphate mixture are blended in a Waring blender and extruded in a 28 mm Werner Pfleiter extruder (rear, 540°F.; front 555°F.; die, 550°F.). The extruded pellets are again extruded under the same conditions and then molded into standard test bars on a 3 oz Newbury injection molding machine (nozzle, front, rear, all 450°F.; die, 170°F.). For comparison purposes, a second composition is made in exactly the same way except that half the mesityl xylyl phosphate mixture is replaced with 65 g of triphenyl phosphate and a third composition is made with 130 g of a commercial grade of isopropylphenyl phosphate mixture.

Test bars 1/16" thick of all compositions are tested for flammability, igniting the bars in a gas flame and measuring the time required for extinction of the flame in each bar according to the procedure of the U.L. 94 test, as modified. The molded pieces are also subjected to physical property measurements, the heat distortion temperature being measured by ASTM method D-648.

The results of the flame test on 5 bars and the physical properties are set forth in Table 1:

TABLE 1
Flammability and Physical Properties of
Polyphenylene Ether and Polystyrene Compositions
Containing The Mesityl Xylyl Phosphate Mixture

Composition	A	B	C
Formulation (parts by weight)			
poly(2,6-dimethyl-1,4-phenylene)ether	400	400	400
high impact polystyrene	600	600	600
mesityl xylyl phosphate mixture	130	65	—
triphenyl phosphate	—	65	—
tri isopropyl phenyl phosphate	—	—	130
decyl diphenyl phosphite	5	5	5
polyethylene	15	15	15
Flame Test			
Average time to extinction (sec.) 1st ignition	14	12	9
Average time to extinction (sec.) 2nd ignition	8	10	14
Physical Properties			
Heat distortion temp., °F at 264 psi	204	195	184
Melt viscosity at 540°F and 1500 sec^{-1}	1400	1200	1150
Notched Izod Impact, ft.lbs./in.	3.3	3.3	2.6
Yellowness Index	32	32	28

Composition A according to this invention, has a significantly higher heat distortion temperature and is comparable in other properties.

EXAMPLE 2

Poly(2,6-dimethyl-1,4-phenylene)ether, 550.0 parts, 450.0 g. of rubber modified high impact polystyrene, 15 parts of polyethylene, 10 parts of diphenyl decyl phosphite, 1.5 parts of zinc sulfide, 1.5 parts of zinc oxide and 35 parts of the mesityl xylyl phosphate mixture are extruded and molded as described in Example 1. A second composition is prepared in the same way except that the half mesityl xylyl phosphate mixture is replaced by 18 parts of triphenyl phosphate and a third composition is prepared from 35 parts of triphenyl phosphate.

The average flame-out time (U.L. 94 test, first ignition) is measured on five 1/16" thick bars, and the physical properties, including heat distortion temperature, are measured. The results are set forth in Table 2:

TABLE 2
Flammability and Physical Properties of
Polyphenylene Ether and Polystyrene Compositions
Containing The Mesityl Xylyl Phosphate Mixture

Composition	D	E	F
Formulation (parts by weight)			
poly(2,6-dimethyl-1,4-phenylene)ether	550	550	550
high impact polystyrene	450	450	450
mesityl xylyl phosphate mixture	35	18	—
triphenyl phosphate	—	17	35
polyethylene	15	15	15
diphenyl decyl phosphite	10	10	10
zinc sulfide	1.5	1.5	1.5
zinc oxide	1.5	1.5	1.5
Flame Test			
Time to extinction (sec.) average of 5, 1st ignition	14	17	17
Physical Properties			
Heat distortion temp., °F. at 264 psi.	245	237	236
Melt viscosity at 540°F and 1500 sec^{-1}	2290	2400	2550
Yellowness Index	31	29	29
Notched Izod Impact, ft.lbs./in.	2.9	3.7	2.5

Compostion D according to this invention, has a significantly higher heat distortion temperature and is comparable in other properties.

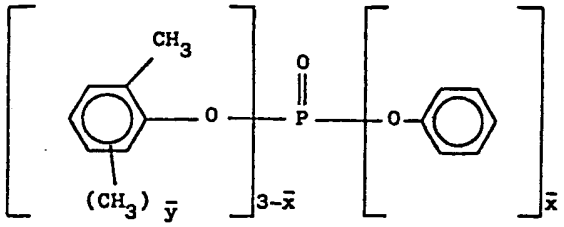
It is obvious that modifications can be made in light of the above examples. For instance, poly(2,6-diphenyl-1,4-phenylene)ether can be substituted for the poly(2,6-dimethyl-1,4-phenylene)ether. For the rubber modified high impact polystyrene, there can be substituted homopolystyrene or a 80:20 copolymer of styrene and methyl methacrylate.

In addition, the compositions of this invention may be formulated with other additives, for conventional purposes, such as pigments, plasticizers, fillers, reinforcements and the like. Furthermore, third component resins such as polyethylene may be added in minor concentrations without departing

from the spirit or scope thereof. The compositions are useful to form films, fibers, molded articles, and the like, in accordance with conventional practice.

CLAIMS

1. A flame retardant mixture comprising a mixture of aromatic phosphates represented by the average formula:



where $\bar{x}$ is a whole or fractional number from slightly more than 0 to slightly less than 3 and $\bar{y}$ is a whole or fractional number from 1 to 2.

2. A mixture as claimed in Claim 1 which comprises at least 2 compounds selected from (a) triphenyl phosphate (TTP), (b) diphenyl mesityl phosphate (DPMP), (c) dimesityl phenyl phosphate (DMPP) and (d) trimesityl phosphate (TMP), at least one of said two compounds being DPMP or DMPP.

3. A mixture as claimed in Claim 1, wherein $\bar{y} = 1$, which comprises at least 2 compounds selected from (a) trixylyl phosphate (TXP), (b) dixylyl mesityl phosphate (DXMP), (c) dimesityl xylyl phosphate (DMXP) and (d) trimesityl phosphate (TMP) at least one of said 2 compounds being DXMP or DMXP.

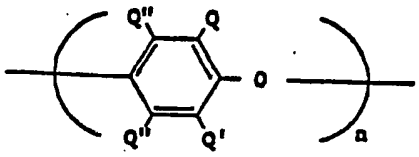
4. A mixture as claimed in any preceding Claim which additionally includes tri(isopropyl phenyl) phosphate.

5. A mixture as claimed in Claim 1 and substantially as hereinbefore described.

6. A resinous composition comprising (a) a normally flammable resinous material and (b) a flame retardant amount of the flame retardant mixture of any one of Claims 1 to 5.

7. A resinous composition as claimed in Claim 6 wherein the normally flammable resinous material comprises

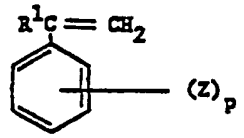
(i) a polyphenylene ether of the formula



wherein the oxygen ether atom of each unit is connected to the benzene nucleus of the next adjoining unit; Q is hydrogen, a hydrocarbon radical, a halohydrocarbon radical having at least two carbon atoms between the halogen atom and the phenol nucleus, a hydrocarbonoxy radical, or a halohydrocarbonoxy radical having at least two carbon atoms between the halogen atom and the phenol nucleus; Q′ and Q″, which can be the same or different, are the same as Q or can be halogen, with the proviso that Q, Q′ and Q″ are all free of a tertiary alpha-carbon atom, and n at least 50; and

(ii) a styrene resin.

8. A resinous composition as claimed in Claim 7 wherein the styrene resin is present in an amount of from 80 to 20% by weight of the weight of components (i) and (ii) in the composition, and has at least 25% by weight of units derived from a vinyl aromatic compound of the formula



wherein R^1 is hydrogen, alkyl or halogen, Z is vinyl, halogen or alkyl and p is 0 or a whole number equal to the number of replaceable hydrogen atoms on the benzene nucleus.

9. A resinous composition as claimed in any of Claims 6 to 8 wherein the flame retardant mixture amounts to 0.5 to 15 parts by weight per 100 parts by weight of the normally flammable resinous material.

10. A resinous composition as claimed in Claim 9 wherein the flame retardant composition amounts to 1 to 10 parts by weight per 100 parts by weight of the normally flammable resinous material.

11. A resinous composition as claimed in any one of Claims 7 to 10 wherein the polyphenylene ether is poly(1,6-dimethyl-1,4-phenylene)ether.

12. A resinous composition as claimed in any one of Claims 7 to 11 wherein the styrene resin is a rubber-modified high impact polystyrene.

13. A resinous composition as claimed in Claim 6 and substantially as hereinbefore described with reference to either of the Examples.

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